LBNL #48667

Invited article for the

33rd IUVSTA Workshop and IV Brazilian Meeting on Diamond, Diamond-Like, Nanotubes, Nitrides and Silicon Carbide
November 28th – 30th, Sao Paulo, Brazil

Synthesis, properties and applications of pure and covalently doped DLC films prepared by energetic condensation.

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November 2001

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This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098

Synthesis, properties and applications of pure and covalently doped DLC films prepared by energetic condensation.

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Abstract:

Hyper-thermal species have been used to produce carbon-based films with mechanical and tribological properties that have greatly expanded the applications of amorphous carbon coatings. Tetragonally bonded amorphous carbon films have properties that approach that of diamond in several ways. The major drawback, namely intrinsic stresses, preventing the production of thick ta-C films has been overcome by heat treating these films, and presently several micrometer-thick films of ta-C are regularly produced. Yet another area where superhard coatings are of great interest is for wear applications at elevated temperatures, namely around 500^{o}C and above. Such temperatures may be environment temperatures, or localized (flash) temperatures resulting for instance from wear. For this applications, doping the ta-C with elements that are covalently bonded to C (such as Si and B) offers a promising alternative. In this article, I will discuss some treatments that have allowed expanding the applications of pure ta-C, and the incorporation of Si and B on ta-C films. Film properties are presented and discussed.

Introduction:

The pioneering work of Aisenberg and Chabot on hard and transparent carbon films prepared by non-mass separated 40 eV carbon ions in 1971 has probably initiated the extensive research and development in hard-carbon films and subsequently in superhard materials. In the ensuing decades, several thin film deposition methods were developed for the production of carbon-base films with outstanding mechanical properties [1]

The most widely used deposition techniques for preparing hard non-hydrogenated carbon films are Mass Selected Ion Beam Deposition (MSIB), Pulsed Laser Deposition (PLD) and Filtered Cathodic Arc (FCA). MSIB is capable of producing high quality films [2-6], although it is not a technology that is expected to gain commercial application. PLD has been also successfully used to prepare high quality DLC films [7,8], although in its current embodiment, it is not expected to have any significant commercial impact. Sputtering for hydrogen free carbon films was introduced by Savvides [9] using an unbalanced magnetron system. Subsequent improvements to this technique allowed the deposition of amorphous carbon films with density over 3 $g.cm^{-3}$ [10]. Filtered cathodic Arc is at this juncture the most promising technique for large-scale production, since it is capable of depositing over large areas with a reasonably fast deposition rate. In contrast with the low ion current density or MSIB(< 100 microA/sqcm), cathodic arc systems can achieve much higher ion current densities, and scaling up to large areas is relatively straightforward [11,12].

DLC films can be grouped in two major classes: hydrogenated and non-hydrogenated. Due to the ubiquitous nature of hydrogen, it is very rare to find films that are truly hydrogen-free, and therefore "non-hydrogenated" in general means that the deposition process does not involve hydrogenated species, and the H content in the film is low, usually below 5%. Table 1 provides a comparison of the properties between hydrogenated and non-hydrogenated DLC:

Table 1: DLC structure, composition and properties

Variable	a-C	a-CH
Hydrogen content	<5	20 - 60
sp^3, %	5 – 85	20 – 65
Density (g cm^{-3})	1.9 – 3.0	0.9 –2.2
Thermal Stability	< 600°C	< 400°C
Optical Gap (eV)	0.4 – 1.5 (? – see my data))	0.8 – 4.0
Index of refraction	1.8 – 2.4	1.8 –2.4
Compressive Stress	< 10 GPa	< 5 GPa
Hardness	< 80 GPa	< 50 GPa
Young's Modulus	< 900 GPa	< 300 GPa
Coefficient of Friction		

The properties of DLC films are strongly dependent on the deposition process conditions, which when optimized can produce films with sp^3 content as high as 85% resulting in amorphous carbon films with properties approaching that of crystalline diamond. In order to achieve a high content of sp^3 bonds, it is recognized that the energy of the depositing ions must exceed 30 eV, a threshold for the C^+ ions to penetrate the surface of the growing film [13-15]. If the energy flux into the growing film is too high, conversion of sp^3 into sp^2 bonded carbon occurs due to either the localized increase in temperature or ion damage.

There is a direct correlation between the properties and the sp^3 content in *ta*-C films [15-19]. The as-deposited DLC films with highest sp^3 content have very high levels of intrinsic stresses, above 10 GPa, which severely limits their maximum useful thickness before delamination occurs. The upper limits for the thickness of such films was found to be between 100 to 200 nm [11,20] . In order to deposit films thicker than 100 nm it becomes necessary to "atomically stitch" the interface by carrying out the deposition using species (atoms or ions) with higher energy at the early stages of the process, or using an intermediate layer that promotes adhesion. The high levels of stresses present in the films with highest sp^3 prevent achieving thickness greater than 500 nm even when such practices are implemented. Therefore thicker films will demand lower intrinsic stresses.

In addition to pure DLC, there is growing interest in doping these films with metallic and non-metallic elements. The major motivation for such investigation are to enhance the properties of the films at elevated temperature; to decrease the level of internal stresses in the film, while preserving the high hardness; to alter the surface tension of the films, and therefore change its wetting characteristics; to alter the electronic properties; and alter the coefficient of friction.

This article reviews some of the current status of the development of the non-hydrogenated amorphous carbon films with high sp^3 content. It also reports on the synthesis and properties of B and Si doped DLC.

2.0 Experimental Procedure:

2.1 Deposition of DLC Films

The deposition technique used in this investigation is known as Metal Plasma Immersion Ion Implantation and Deposition. Undoped DLC was deposited from a filtered cathodic arc plasma source using a graphite cathode. The compound films were prepared using two FCA sources: one source used a graphite cathode, and the other source used a cathode made of Si. In the case of the DLC:B films, the film was produced by mixing a plasma stream from a B_4C cathode with that of a graphite cathode. The undoped DLC and the DLC:Si were prepared using LBNL's small, repetitively pulsed vacuum arc plasma guns operated at a pulse length of few milliseconds and repetition rate of 1 Hz. In order to remove macroparticles, a 90^o filter was used. The substrate was negatively to control the energy of the incident ions.

For the deposition of DLC:Si a highly doped silicon cathode was used in order to start and sustain the arc. In the case of B_4C, a more stable arc was obtained when the cathode was heated to approximately 600^oC in order to enhance its electrical conductivity. In the case of the films with Boron, no filter was used.

2.2 Chemical and Structural Characterization

Film composition was investigated by several techniques. X-ray absorption spectroscopy (NEXAFS) was also carried out to look at the near-surface chemistry of these films. NEXAFS spectra were taken using synchrotron radiation at the beam 7.3.1.1

at the Advanced Light Source. This is a bending magnet beamline that covers the 175 – 1500 eV spectral range, which contains the K-edges of the light elements (B, C, O, N and F), the L-edges of the 3d transition metals and the M_{4-5}-edges of the rare-earths [21] . A graphite and a diamond crystal were used as sample references for the energy calibration. The NEXAFS spectra were taken in a total electron yield mode by measuring the current from the sample to ground. The angle of incidence of the beam was set to be 57^{o}. This angle prevents any polarization of the X-Ray. Under the experimental conditions, the depth sensitivity is approximately 7 to10 nm. The analyzed samples were exposed to air between the time they were prepared and the analysis. In order to preserve the bonding state of the films analyzed, no annealing was carried out prior to the analysis, and therefore the interpretation of the observed peaks required considering possible surface contamination.

Electron microscopy (transmission and scanning) was used to characterize the morphology and structure of the films. TEM was carried out in a Phillips CM200 with a PEELS (Parallel Energy Loss Spectroscopy) system and a Topcon 002B with point resolution of 0.19 nm at 200 kV. Morphology was investigated using a JEOL6400 scanning electron microscope. Quantitative composition analysis was performed in a Rutherford Backscattering Spectroscope using a 1.8 keV He^{+} beam.

2.3 Mechanical Characterization

Hardness and elastic modulus of the films were determined by nanoindentation using a Hysitron Picoindenter. The hardness was evaluated from the residual impression of the

indenter whereas the modulus was determined from the slope of the load-unload curve at the beginning of the unloading process. Friction coefficient was also determined by using a Hysitron Nanoscope measuring the lateral force for different vertical loads.

Intrinsic stresses were determined using the curvature method and Stoney's equation. Thin wafers were used and the curvature measured before and after the deposition of the film.

3.0 Results and Discussions:

3.1 Undoped DLC:

The correlation between the substrate bias voltage, which corresponds to the depositing ion energy, and the film properties is shown in Figures 1 through 3. Figure 1 shows the hardness of undoped DLC prepared at different bias voltages. The applied bias voltage is actually pulsed with a duty cycle of 25%. Duty cycle here is defined as the ratio on-time:off-time of the bias voltage. Figure 2 shows the intrinsic stresses of the same films. Figure 3 shows the sp^3 content as a function of the applied bias voltage. It is readily observed that the maxima in intrinsic stresses, hardness and sp^3 content are all obtained for the same bias voltage. This is in agreement with previous investigations[11, 14-17]. The exact voltage corresponding to the maximum in sp^3 may vary slightly from process to process, depending among other things on the ion flux and thermal load on the substrate.

3.2 Si doped DLC:

Si–doped DLC films with Si content ranging from 3 to 5 at.% were prepared for this work using a dual source filtered cathodic arc. The films were amorphous and also have significant intrinsic compressive stresses. Presence of compressive stresses can be seen by the characteristic wave pattern seen in the image shown in Figure 4. Figure 4 is a transmission electron image of a free standing DLC:Si with 5 at.% Si. This film was prepared using a bias voltage of –100 V and duty cycle of 25%. These conditions were the same used to prepare the undoped DLC with highest sp^3 content.

Hardness and elastic modulus are strongly dependent on the Si content. Figure 5 shows the hardness obtained for several indentation loads for the three compositions of DLC:Si. Increasing the load allows probing the hardness at greater depths into the film, which may very if there is non-uniformity on structure or bonding which depend on the thickness. Comparing Figures 1 and 5, it can be seen that the hardness of the 3 at% Si is only slightly smaller than the hardness of the undoped material prepared with the same bias voltage. As the Si content increases even further, hardness decreases to values around 40 GPa to 45 GPa. Hardness values of DLC:Si with 5 at.% and 6 at.% were virtually the same. On the contrary, although the elastic modulus was also observed to follow the same trend, there was a greater difference between the modulus of the samples with 5 at.% and 6 at.%. The decrease in modulus seems to be more sensitive to small changes in Si content than the decrease in hardness.

The bonding structure of the Si doped DLC was qualitatively inferred from the X-ray absorption spectra shown in Figure 6. In addition to the absorption spectrum for the

DLC:Si, Figure 6 also shows the spectrum obtained from the undoped DLC. Three main peaks are observed in the undoped material are around 284 to 290 eV. The peak at 285.1 eV corresponds to the transition $C1s \rightarrow \pi^*$ for the sp^2 C=C bond. The peak at 286.9 corresponds to the transition $C1s \rightarrow \pi^*$ for the sp^2 C=O bond. Since this technique only probes the top 10 nm of the film, adsorbed species may have a disproportional contribution to the spectrum. The most interesting peak however is the one at 289.0 eV, which has been associated to the presence of excitons in sp^3-rich material. The change in intensity of the absorption peak at 289 eV in the DLC:Si shows a significant increase with addition of Si when compared to the undoped DLC, indicating that this element leads to an increase in sp^3 bonded C.

The coefficient of friction (COF) of DLC:Si in normal atmosphere (RH about 30%) was relatively insensitive to the Si content for the small concentrations of Si tested here. The COF varied from about 0.05 for the lowest loads (50μN) up to 0.25 for the largest loads (500 μN). The low values, obtained with the smallest loads, are more representative of COF, since the amount of plastic deformation and wear is minimized. For the sake of comparison, the COF of undoped DLC prepared by filtered cathodic arc is between 0.1 and 0.2, depending on the content of sp^3 bonds in the film.

3.3 B doped DLC and B_4C:

The preparation of DLC:B and B_4C required a different plasma source because of the small conductivity of B and B_4C at room temperatures. Therefore a plasma source, which makes use of an externally heated cathode had to be used. This source is still being

developed and had no macroparticle filter. Therefore the films containing films have a significantly larger amount of macroparticles than the undoped or Si-doped DLC.

A scanning electron micrograph of a typical B_4C film prepared with the heated cathode source is shown in Figure 7. Macroparticles are readily visible in the films as humps. The films consist of a mixture of amorphous and crystalline phases. Hardness of amorphous B_4C is typically lower than hardness of crystalline B_4C, which at room temperature are about 30 GPa. Here however, we observed a dependence of hardness on the applied bias voltage, which is consistent with the sub-plantation model. Hardness without any bias voltage was 15 GPa , which increased to 25 and 26 GPa at bias voltages of –100V and –500V. The COF for these films was higher than the COF for DLC or DLC:Si. Values of COF for B_4C oscillate between 0.3 and 0.4. Since these films were significantly rougher than the DLC and the DLC:Si, surface roughness may play an important role in increasing the COF.

Similarly to the observation with the DLC:Si, the amount of sp^3 bonded carbon appears to increase with increasing the B content in the films, as observed by X-ray absorption experiments. Figure 8 shows the spectrum of a DLC:B with 5 at.% B and that of a B_4C film. Small addition of B also promote the increase in intensity of the exciton peak at 289 eV, when comparing Figures 6 and 8. Moreover, Figure 8 also indicates that the π^* peak virtually vanishes, and the intensity of the exciton peak increases, suggesting that the C in B_4C is primarily sp^3 bonded.

4.0 Summary and Conclusions:

The properties of non-hydrogenated DLC films prepared by filtered cathodic arc are strongly dependent on the bias voltage applied to the substrate during the deposition process. At the optimum voltage of –100 V, the amount of sp^3 in the films is maximum, and the hardness and intrinsic stress are also maximized. Addition of doping elements such as Si and B are known to decrease the stress level in these films, and to increase their thermal stability.

Addition of Si in small quantities lead to a slight decrease in the hardness of these films. X-ray absorption has shown that the amount of sp^3 bond in these films increases with the addition of Si. The coefficient of friction of DLC:Si ranges from 0.05 to 0.25. B incorporation to DLC also leads to increasing the sp^3 content and the properties of DLC:B are also dependent on the applied bias voltage.

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Figure 1: Hardness of DLC films prepared using several bias voltages applied to the substrate

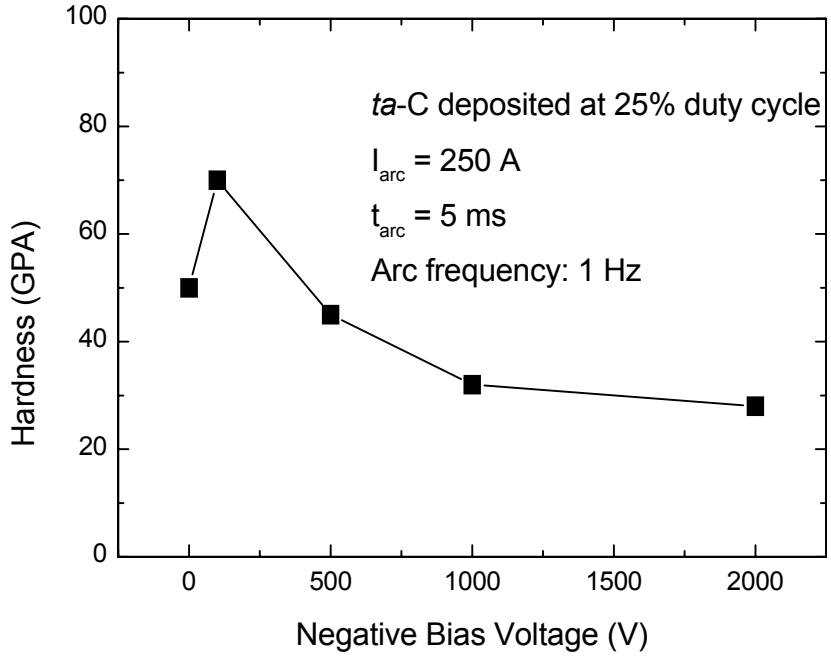

Figure 2: Intrinsic stress in DLC films prepared using several bias voltages applied to the substrate

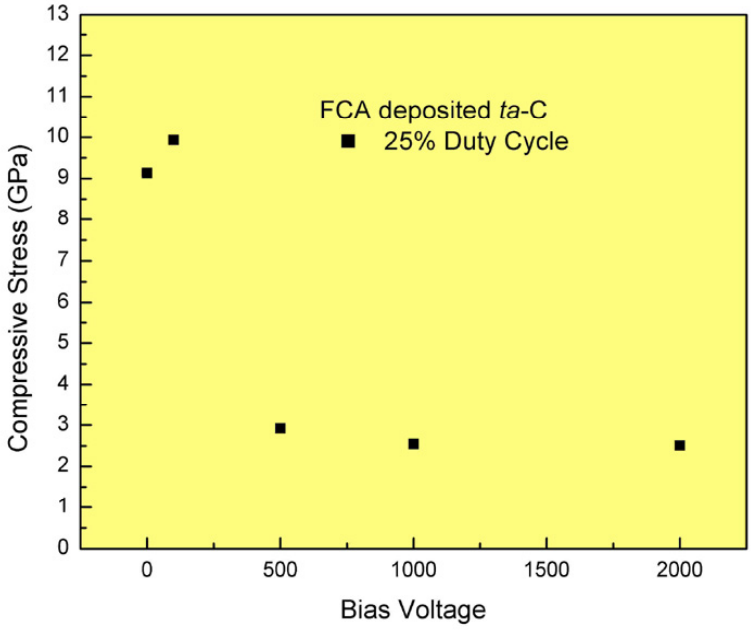

Figure 3: Sp^3 content of DLC films prepared using several bias voltages applied to the substrate

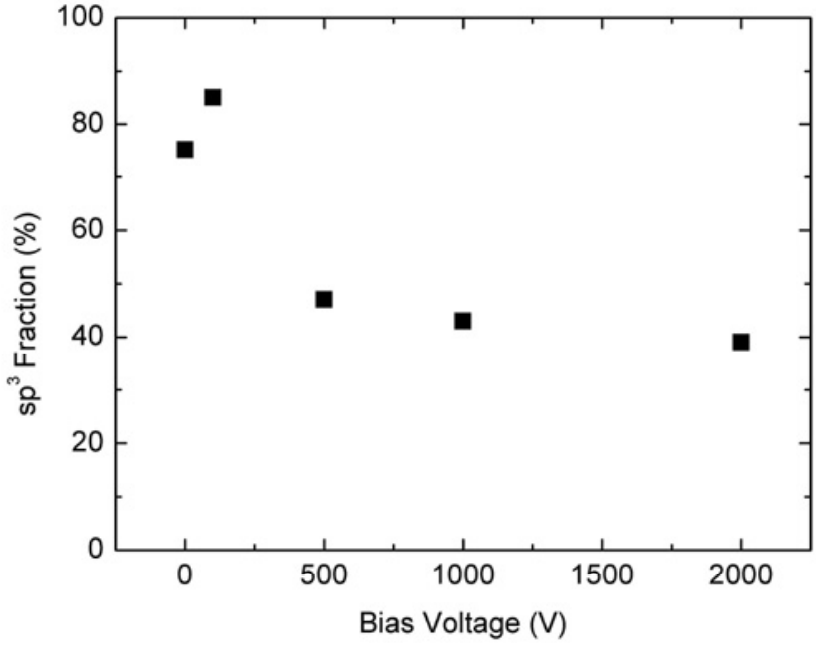

Figure 4: Transmission electron micrograph of free-standing DLC:Si with 5 at.% Si. The film is very uniform, and the wave pattern are typical of films under compressive stress

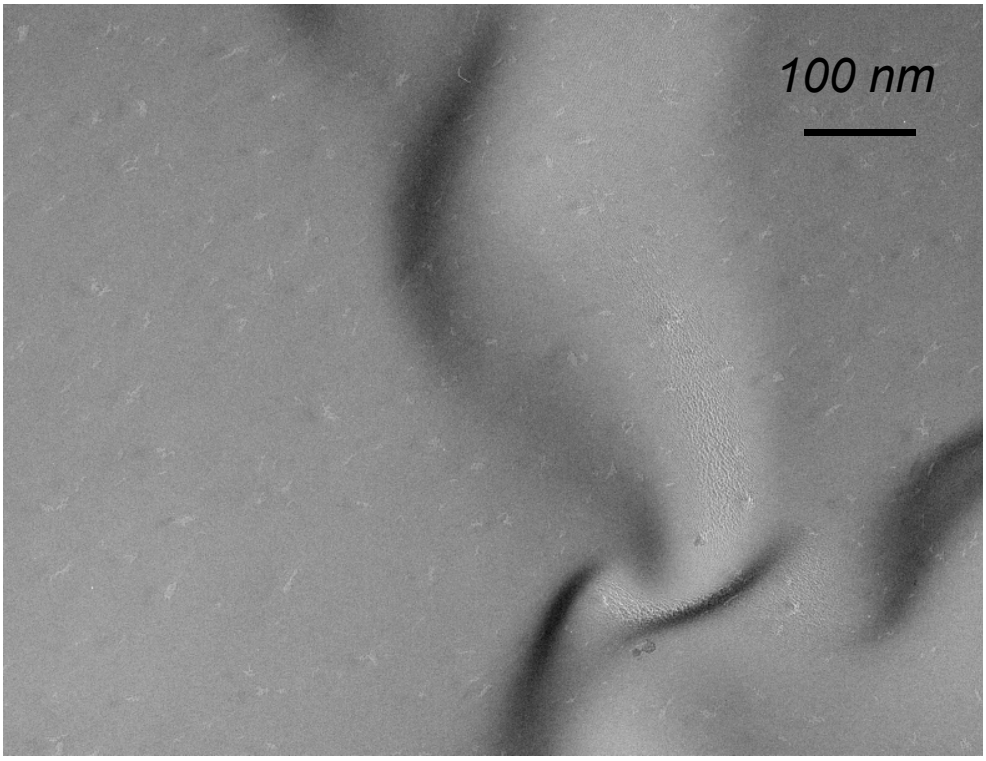

Figure 5: Hardness of DLC:Si films with Si contents of 3, 5 and 6 at.%

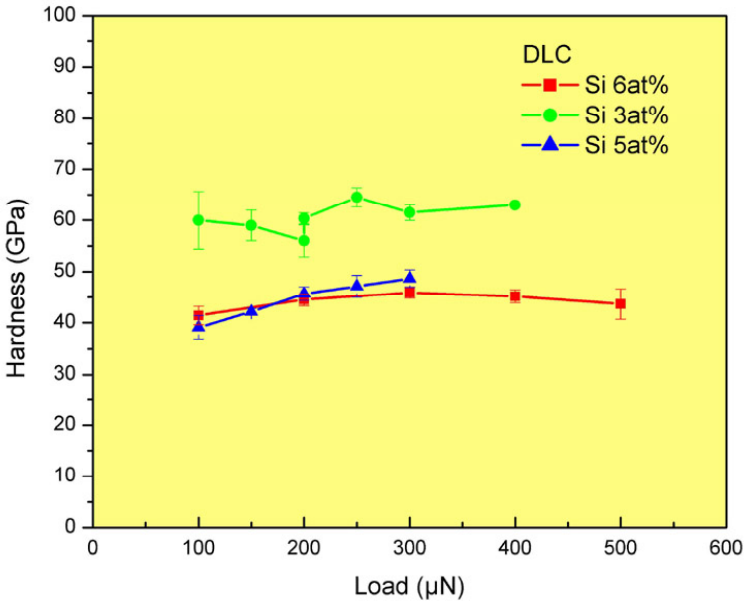

Figure 6: X-ray absorption spectra of undoped DLC and DLC:Si. The electronic transitions associated with the most important peaks are indicated in the figure

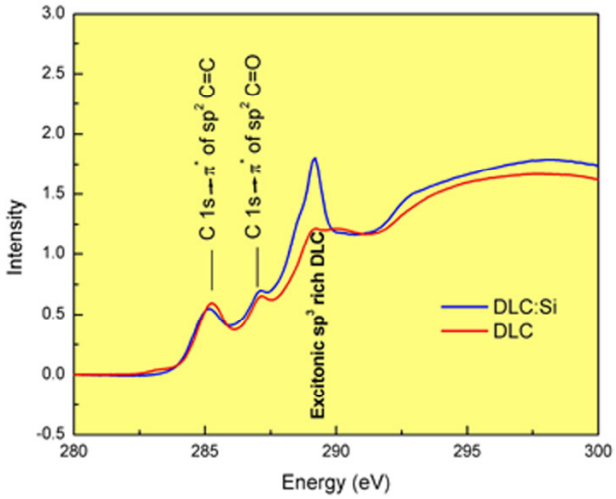

Figure 7: Scanning electron micrograph of B_4C prepared by unfiltered cathodic arc

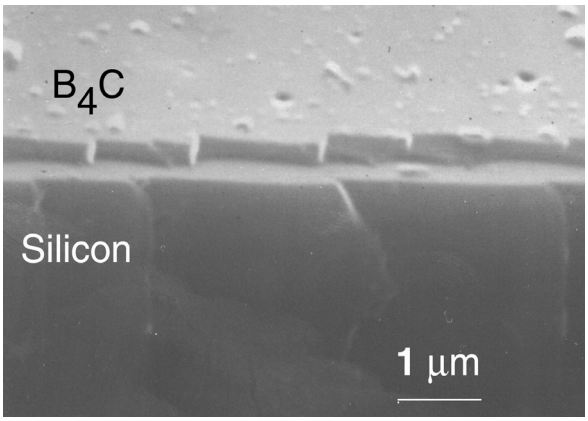

Figure 8: X-ray absorption spectra of undoped B_4C and DLC:B.